

# Effects of phase transformation on photoluminescence behavior of ZnO:Eu prepared in different solvents

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Received 26 August 2004; received in revised form 30 October 2004; accepted 22 November 2004

Available online 24 February 2005

## Abstract

Europium doped zinc oxide (Eu:ZnO) powder has been prepared by mixing ZnO and Eu<sub>2</sub>O<sub>3</sub> in deionized water and acetone solvents. The influence of phase transformation of Eu-doped ZnO powders mixed in different solvents on the luminescence behavior has been investigated. When the powder was mixed in deionized water and then sintered at high temperatures, Eu<sup>3+</sup> ions were detected in the ZnO matrix. The intrinsic red photoluminescence (<sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>) of Eu<sup>3+</sup> was easily shielded by the ZnO intrinsic defect as the samples were excited with 325 nm short wavelength as a consequence of the energy level of Eu<sub>Zn</sub><sup>•</sup> (0.19 eV) being closer to conduction band than the one of Zn<sub>i</sub><sup>••</sup> (0.22 eV). Therefore, no red emission can be detected. In contrast, as the Eu-doped ZnO powder was mixed in acetone solvent (without OH<sup>-</sup>), no Eu<sup>3+</sup> ions could be detected in the ZnO matrix. In addition, the red emission could be detected not only under excitation with long wavelength (532 nm) but also at short wavelength (325 nm).

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**Keywords:** A. Mixing; C. Optical properties; D. ZnO; Eu<sub>2</sub>O<sub>3</sub>

## 1. Introduction

Wide band-gap materials always present good potential for full color phosphors [1]. Zinc oxide is one of the wide band-gap materials and shows versatile applications [2–4]. However, a pure red emission could not be obtained since the sharp red emission was also accompanied by a broad green emission due to self-activated centers. It is well known that zinc oxide easily produces intrinsic defects such as interstitial zinc (Zn<sub>i</sub><sup>••</sup>) and oxygen vacancy (V<sub>o</sub><sup>••</sup>). These defects will influence the photoluminescence behavior of ZnO in different ways [5]. The emission characteristics of ZnO doped with various impurities have been extensively studied [6–8]. Depending on the relative energy of the 4f emitting level, the excitation of RE<sup>3+</sup> is either a direct 4f–4f process or an indirect process. However, it has been reported

that the 4f–4f electron emission of trivalent RE<sup>3+</sup> in the ZnO lattice is extremely difficult under UV excitation. Recently, Hayashi et al. [9] and Park et al. [10] have observed a red emission of Eu<sup>3+</sup> ions from complete quenching of the EuCl<sub>3</sub>-doped ZnO phosphors sintered in vacuum. It was claimed that the red emission is due to an energy-transfer process occurring from the self-activated defect centers in ZnO host to the Eu<sup>3+</sup> ion which exists in the form of EuOCl. The addition of a co-activator such as Li<sup>+</sup> is also used to promote the photo-excited RE<sup>3+</sup> luminescence, while no apparent enhancement in the luminescence intensity of the Eu<sup>3+</sup> was obtained. In addition, it was reported that the existence of OH<sup>-</sup> from the solvent will retards the emission of RE<sup>3+</sup> [11]. Therefore, more information is required for successfully developing ZnO:Eu for application in field emission displays (FED).

Several attempts were undertaken to obtain a strong red luminescence from ZnO:Eu, especially the role of solvent and processing temperature in the luminescence behavior of

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ZnO/RE<sup>3+</sup>. In this work, two solvents, deionized water and acetone, were used to study the phase transformation of Eu-doped ZnO powder in terms of ball-milling and sintering temperature. The effect of phase transformation on the luminescence behavior of ZnO/RE<sup>3+</sup> was also elucidated.

## 2. Experimental procedures

Europium doped zinc oxide (Eu:ZnO) powder was prepared by mixing 99.99 purity ZnO and Eu<sub>2</sub>O<sub>3</sub>. The powder mixture was ball-milled in a polyethylene ball with Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> grinding media in both deionized water (with OH<sup>-</sup>) and acetone (without OH<sup>-</sup>) solvents. After dried, the powder was then sintered at different temperature (600–1000 °C) for 1 h in air and subsequently cooled to room temperature. The crystal phases have been detected by X-ray diffraction (XRD) (MAC Science, M18X) (Tokyo, Japan) with Cu K $\alpha$  radiation. Luminescent properties at room temperature have been characterized by photoluminescence (PL) measurements under 325 nm and 532 nm excitation wavelength ( $\lambda$ ) (FL F4500, Hitachi). The surface microstructure and chemistry were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

## 3. Results and discussion

### 3.1. OH<sup>-</sup> effect

Prior to ball-milling in deionized water, pure Eu<sub>2</sub>O<sub>3</sub> powder is a cubic structure according to XRD patterns in Fig. 1(a). However, after ball-milling, it was found that cubic Eu<sub>2</sub>O<sub>3</sub> powder was transformed into hexagonal Eu(OH)<sub>3</sub> as shown in Fig. 1(b). In order to check OH<sup>-</sup> effect, acetone instead of deionized water was used in the ball-milling but

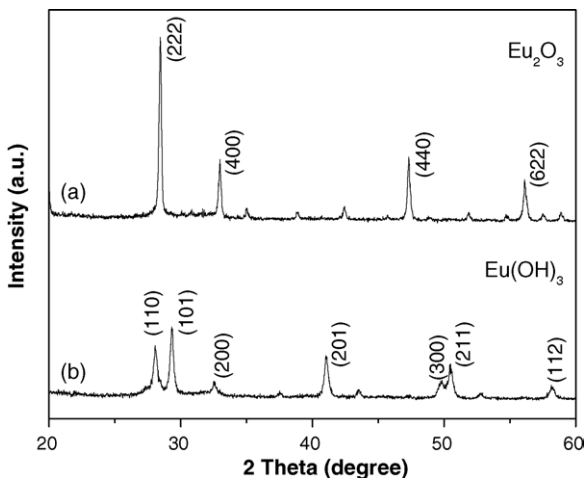


Fig. 1. XRD patterns of the Eu<sub>2</sub>O<sub>3</sub> powder (a) without and (b) with ball-milling in deionized water.

no apparent difference was detected. Therefore, it can be assumed that the existence of OH<sup>-</sup> ion promotes the formation of the Eu(OH)<sub>3</sub> phase. Park et al. [10] studied the photoluminescence characteristics of ZnO:EuCl<sub>3</sub> phosphors and found that Eu can exist in the ZnO host lattice as EuOCl, implying the possibility of incorporation of Eu<sup>3+</sup> into the ZnO lattice.

Fig. 2 shows the XRD patterns of 0.5 wt.% Eu-doped ZnO powder mixed in (a) deionized water and (b) acetone, respectively. It was observed that both of them present a different phase evolution as function of the sintering temperature. In deionized water, the peak intensity at  $2\theta = 28.4^\circ$  (corresponding to the Eu<sub>2</sub>O<sub>3</sub> phase) becomes stronger with the sintering temperature (Fig. 2(a)). This phenomenon was tentatively related to the formation of Eu(OH)<sub>3</sub> as evidenced from Fig. 1(b). An increase in the sintering temperature will lead to the decomposition of Eu(OH)<sub>3</sub> and promotes the formation of the Eu<sub>2</sub>O<sub>3</sub> phase. In contrast, in the acetone solvent, the peak intensity of Eu<sub>2</sub>O<sub>3</sub> shown in Fig. 2(b) remains unchanged with the sintering temperature.

The 0.5 wt.% Eu-doped ZnO powder mixed in (a) deionized water and (b) acetone was measured by PL

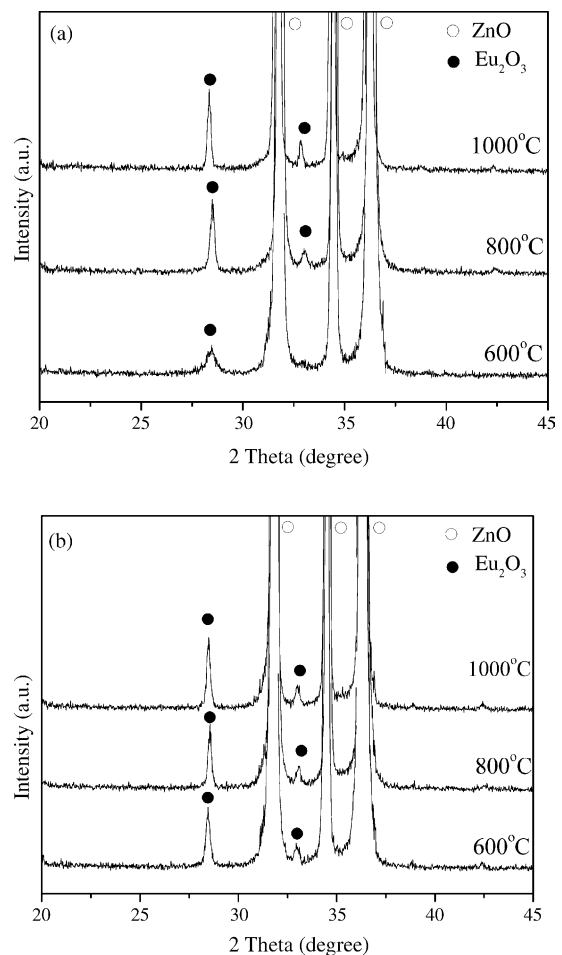


Fig. 2. XRD patterns of 0.5 wt.% Eu-doped ZnO powder mixed in (a) deionized water and (b) acetone and then sintered at 600–1000 °C/h.

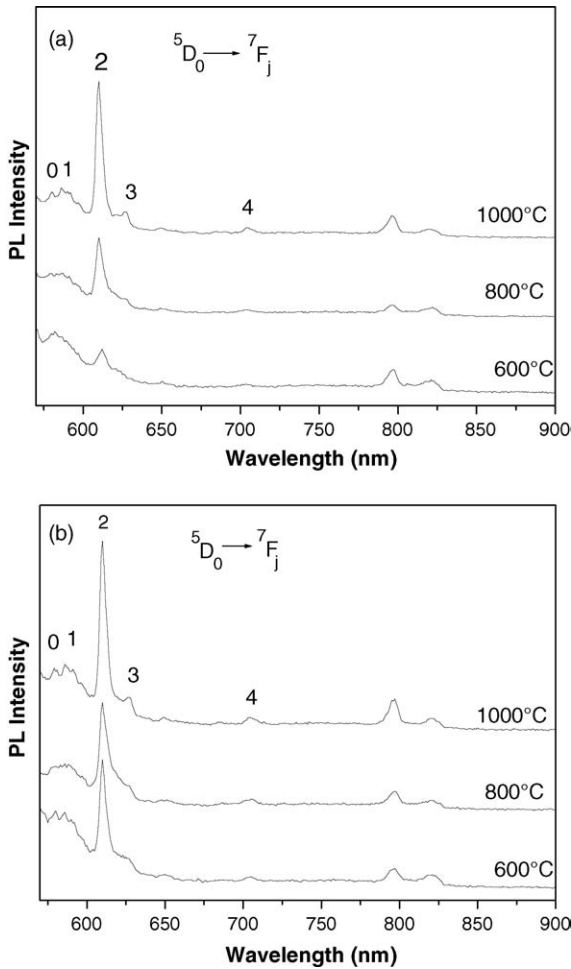


Fig. 3. PL spectra of 0.5 wt.% Eu-doped ZnO powder mixed in (a) deionized water and (b) acetone and sintered in air (excitation wavelength 532 nm).

(excitation wavelength 532 nm). Fig. 3 shows that all PL spectra are characteristic of the main  $\text{Eu}^{3+}$  red emission and this is due to  $\text{Eu}^{3+}$  transition from  $^5\text{D}_0$  to  $^7\text{F}_j$  ( $j=0-4$ ) energy level. The sensitively red PL transition for  $\text{Eu}^{3+}$  is  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ . As illustrated in Fig. 3(a), at low temperatures, the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  of  $\text{Eu}^{3+}$  emission is still influenced by the  $\text{OH}^-$  quench effect and the PL intensity is very weak for the samples mixed in deionized water, in contrast to the sample mixed in acetone. Apparently, the  $\text{OH}^-$  plays an important role in the PL intensity which is consistent with the observation of XRD in Fig. 2. This demonstrates  $\text{OH}^-$  to quench the emission of  $\text{RE}^{3+}$  of the  $\text{ZnO-Eu}_2\text{O}_3$  powder mixed in deionized water.

The emission intensity of  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j=1-4$ ) is also dependent on the sintering conditions. The  $\eta_{21}$  and  $\eta_{41}$  represent the relative intensity ratio of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , respectively, and are listed in Table 1. These two values indicate the degree of short-range order and long-range order of  $\text{Eu}^{3+}$  in the crystal lattice, respectively. For the water-milled sample, the  $\eta_{21}$  value increases with increasing temperature. At a low sintering temperature of 600 °C, the  $\text{OH}^-$  ion diffuses into

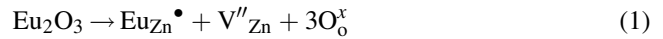
Table 1  
Relative intensity ratio of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  as a function of sintering temperature for ZnO:Eu powders

Sample	Temperature (°C)	Solvent	$\eta_{21}$	$\eta_{41}$
ZnO:Eu 0.5 wt.%	600	Water	0.54	0.43
	800	Water	1.11	0.55
	1000	Water	1.35	0.48
ZnO:Eu 0.5 wt.%	600	Acetone	1.34	0.45
	800	Acetone	1.38	0.478
	1000	Acetone	1.25	0.32
ZnO:Eu 0.2 wt.%	1000	Water	0.65	0.39

$\text{Eu}_2\text{O}_3$  lattice and changes the short-range order and  $\eta_{21}$  value. However, at high temperature,  $\text{Eu}(\text{OH})_3$  will be decomposed and the  $\eta_{21}$  value will be increased. The phenomenon can be used to elucidate why the Eu:ZnO samples show different PL behavior at different sintering temperature in deionized water in comparison with that in acetone (Fig. 3).

### 3.2. Eu amount

The addition of  $\text{Eu}_2\text{O}_3$  may behave as donor through the substitution of Zn-site and promote zinc-site vacancy ( $\text{V}''_{\text{Zn}}$ ) formation as shown below.



Eq. (1) illustrates that the doping effect forms a shadow level ( $\text{Eu}_{\text{Zn}}^\bullet$ ) below the conduction band and increases the conductivity. In order to confirm the possibility of the substitution of Eu for Zn in the ZnO host, magnified XRD patterns of ZnO (1 0 1) peak as a function of Eu amount were studied. As illustrated in Fig. 4, the peak change in the XRD patterns indicates a minor substitution Eu for Zn in the ZnO lattice ( $\text{Eu}_{\text{Zn}}^\bullet$ ) but above 0.2 wt.%, the presence of Eu aggregates was detected from the heavily Eu-doped samples.

Fig. 4 shows that the Eu could substitute for Zn, where even a smaller amount would result in the formation of Zn

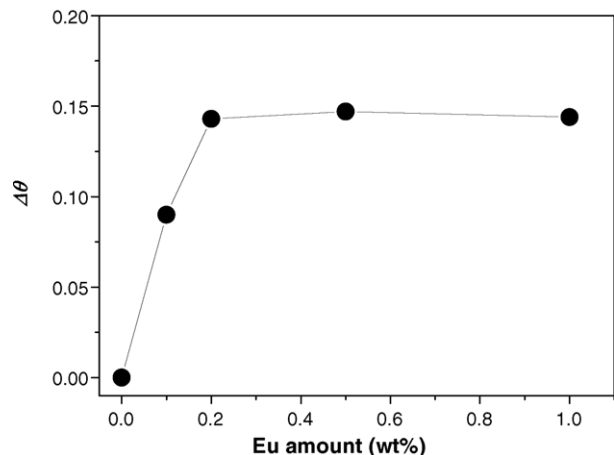


Fig. 4. Peak shift in ZnO (1 0 1) peak as a function of Eu amount.

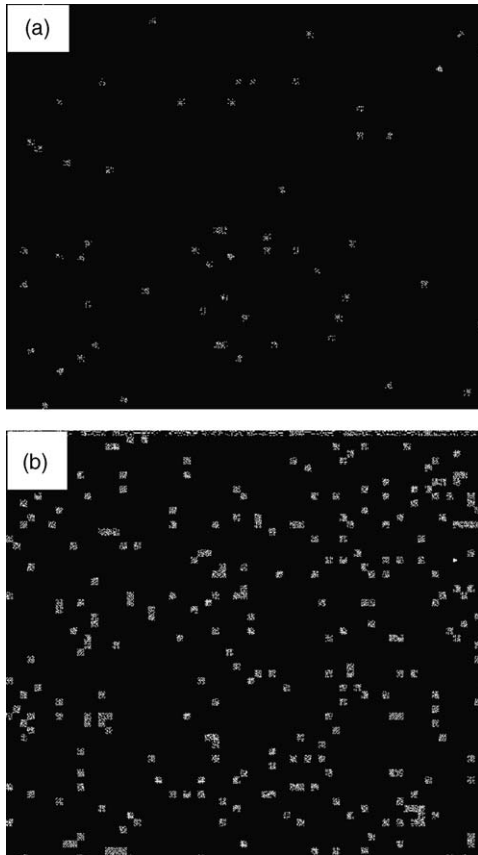


Fig. 5. Eu mapping of the 0.5 wt.% Eu-doped ZnO sample sintered at (a) 600 °C and (b) 1000 °C in air.

interstitials. However, at higher temperatures, Schottky disorder may occur as follows.



More  $\text{V}_{\text{Zn}}''$  defects benefit the reverse reaction of Eq. (1) and decrease  $\text{Eu}_{\text{Zn}}^{\bullet}$  defect concentration. Therefore, the probability of  $\text{Eu}^{3+}$  ion to occupy the  $\text{V}_{\text{Zn}}''$  sites is also decreased, indicating that the solubility of  $\text{Eu}^{3+}$  ion into ZnO lattice will be limited. Therefore, at a higher sintering temperature, more  $\text{Zn}_i^{\bullet\bullet}$  and  $\text{V}_{\text{Zn}}''$  defects will be easily created and this leads to the formation of the  $\text{Eu}_2\text{O}_3$  phase. As evidenced from, The Eu mapping of the 0.5 wt.% Eu-doped ZnO sample (Fig. 5) evidences that with increasing sintering temperature from (a) 600 °C to (b) 1000 °C, more separated  $\text{Eu}_2\text{O}_3$  particles are widely distributed among ZnO grains. However, as the ZnO was doped with less than 0.2 wt.% Eu and sintered at 1000 °C, no separated  $\text{Eu}_2\text{O}_3$  particles were detected among ZnO grains, this indicating that the solution limit in the Eu-doped ZnO system is below 0.2 wt.% Eu, in agreement with the result shown in Fig. 4.

According to the Einstein relations:  $\frac{D_n}{\mu_n} = \frac{D_p}{\mu_p} = \frac{kT}{e}$  and conductivity  $\sigma = e\mu_n n$  (where  $\mu_n$  is the n-type mobility,  $D_n$  the electron diffusion coefficient for n-type semiconductor), the conductivity ( $\sigma$ ) is proportional to  $e^2/T$ . The temperature dependence on conductivity of Eu-doped ZnO can be plotted

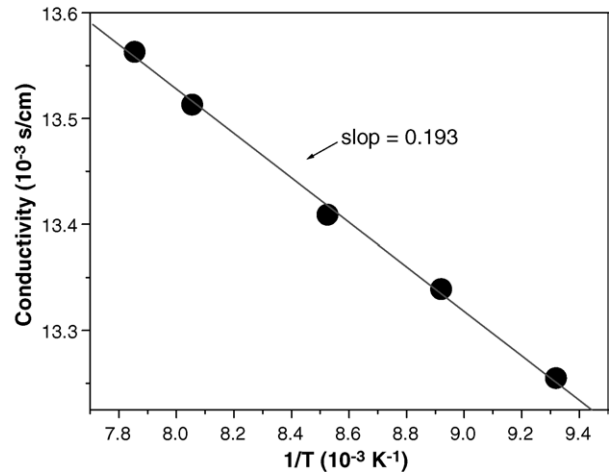


Fig. 6. Temperature dependence on conductivity of Eu-doped ZnO.

and shown in Fig. 6. The slope (energy level of  $\text{Eu}_{\text{Zn}}^{\bullet}$ ) can be calculated to be approximately 0.19 eV below the conduction band, and the energy level is closer to the conduction band than these for  $\text{Zn}_i^{\bullet\bullet}$  (0.22 eV). This indicates that  $\text{Eu}_{\text{Zn}}^{\bullet}$

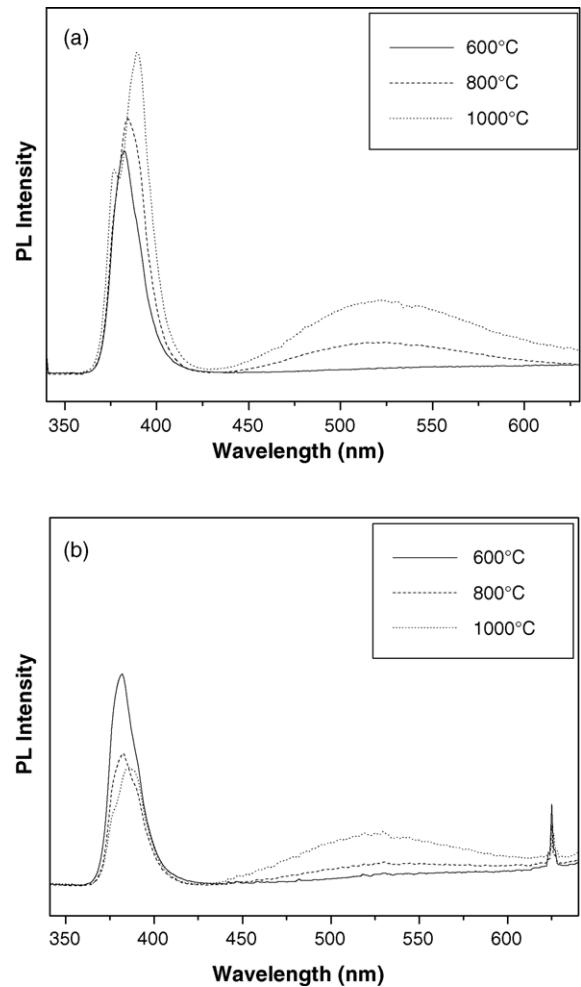


Fig. 7. PL spectra of 0.5 wt.% Eu-doped ZnO powder mixed in (a) deionized water and (b) acetone in air (excitation wavelength 325 nm).

defect may exist in the ZnO lattice and the electrons are jumped easily from the conduction band to  $\text{Eu}_{\text{Zn}}^{\bullet}$  level than to  $\text{Zn}_i^{\bullet\bullet}$  level.

### 3.3. Effect of excitation wavelength

It is well known that when exciting the semiconducting substrate with a wavelength lower than 385 nm, no emission from the rare-earth dopant could be observed. Therefore, as a short wavelength of 325 nm was used to excite the 0.5 wt.% Eu-doped ZnO samples, it was very difficult to observe the red emission of the  $\text{Eu}^{3+}$  from the sample mixed in deionized water. In other words, only broad green (540 nm) and near UV (380 nm) region emissions are observed in Fig. 7(a). The UV emission band is due to ZnO intrinsic emission. The green emission results from zinc interstitials and oxygen vacancy. The disappearance of the red emission excited at 325 nm wavelength is probably related to the shielding effect due to the existence of the  $\text{Eu}_{\text{Zn}}^{\bullet}$  level. In contrast, for the Eu-doped ZnO samples milled in acetone, a red emission can be detected under excitation not only at 532 nm wavelength (Fig. 3(b)) but also 325 nm wavelength (Fig. 7(b)). This may possibly suggest that the generated excitation electron from  $\text{Eu}_2\text{O}_3$  does not completely transfer to  $\text{Zn}_i^{\bullet\bullet}$  site and that no  $\text{OH}^-$  quenching effect occurs in the acetone-mixed sample.

## 4. Conclusions

The phase transformation of Eu-doped ZnO powders prepared in different solvents on luminescence behavior was studied. It was found that the solvent plays a very important role in the ZnO– $\text{Eu}_2\text{O}_3$  system. When the powder was mixed in deionized water, it leads to the existence of  $\text{Eu}^{3+}$  ion in the ZnO matrix. The intrinsic red photoluminescence ( $^3\text{D}_0 \rightarrow ^7\text{F}_2$ ) of  $\text{Eu}^{3+}$  is easily shielded by the ZnO intrinsic defect when the samples were excited with a short wavelength of 325 nm, because the energy level of  $\text{Eu}_{\text{Zn}}^{\bullet}$  (0.19 eV) is closer to the conduction band than for  $\text{Zn}_i^{\bullet\bullet}$

(0.22 eV). Therefore, no red emission can be detected. However, this work demonstrates that a sharp red emission can be promoted by treating the Eu-doped ZnO sample in acetone solvent.

## Acknowledgment

This work was financially supported by the National Science Council of Taiwan under Contract No. NSC-92-2216-E-009-014.

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